

**No. 270 - Methyl 3,4-diphenylcyclopentadienone dicarboxylate:
addition reactions, photooxidation.
3,4-Diphenyl-2-furanone, 3,4-diphenyl-2-pyrrolinone
and the corresponding dehydrodimers**

by

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La photoxydation de la cyclopentadiénone ci-dessus donne le dihydroxy-2,5 diphényl-3,4 dihydro-2,5 furannedicarboxylate de méthyle et ses monoéthers, qui conduisent par hydrolyse et décarboxylation à la diphényl-3,4 furannone-2. Par condensation de celle-ci et de la diphényl-3,4 pyrrolinone-2 avec l'anhydride et l'imide diphénylmaléiques se forment les $\Delta^{2,3'}$ -bifurannédione-5,5' et $\Delta^{2,3'}$ -bipyrrolinedione-5,5' correspondantes.

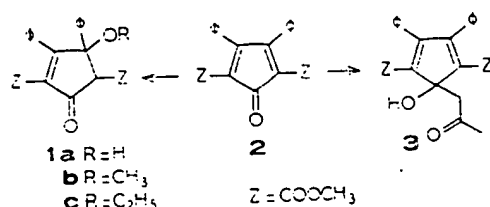
It is known that the photooxidation of cyclopentadienones (tetracyclone and analogs) produces 1,4-(Z)-enediones or o-diketones through peroxides which cannot be isolated (1, 2, 3). In all the cases studied previously, the substituents were alkyl groups or aryl groups. The ketodiester **2** was chosen, which carries two methoxycarbonyl groups, which are electron-attracting groups, unfavorable for reactions of the singlet oxygen. Previously, considering the very pronounced additive properties of the ketodiester **2** (5, 6), reactions of certain solvents were studied (alcohols, acetone) as well as of reducing agents (iodide, thiourea), frequently used for photooxidations. Moreover, since the photooxidation products of **2**, the monohydrate [bis(hemiketal)], **9**, of the expected enedione, **8**, and its monoethers, transform easily into the lactone **13**, as a result of a previous study (4), we were led to the lactam **19** and to its dehydrodimers **22** and **23**.

1) *Addition reactions of cyclopentadienone diester 2*

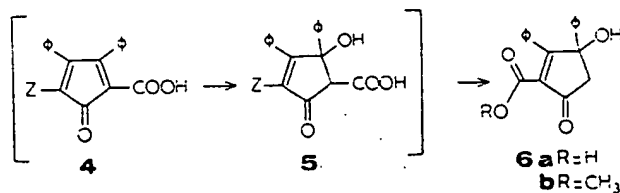
These addition reactions are of two types: 1,2-additions to the carbonyl in a protic medium [dialkylhydrazines (5)] or acidic medium [hydroxylamine, arylhydrazines (6)]; 1,4-additions to an ethylenic bond in an aprotic medium [dialkylhydrazines (5)] or basic medium [water, alcohols (5); primary amines, hydrazine, arylhydrazines (6)].

1,2-Addition in the presence of a specific acid mixture (acetic acid - alkali iodide) is also observed with acetone. The ketol-diester **3** is formed. Iodide in the neutral medium is a poor catalyst and other acid systems (notably acetic acid - sodium bromide) or basic systems are without action. An intermediate brown coloration (which also appears in other solvents) is attributed to an iodine \rightarrow cyclopentadienone charge transfer complex, which may facilitate addition of the enol of acetone to the carbonyl of **2**. Additions of acetone to one of the carbonyls of certain quinones is already known (7). Dehydration of the ketol-diester **3** undoubtedly produces the corresponding fulvene, but this substance is too unstable to be able to be studied.

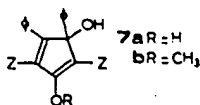
The 1,4-addition of water or alcohols (5), which is very rapid even in a neutral medium, is not accelerated by light. It gives the ketol-diester **1a**, which is an intermediate in the preparation of the ketodiester **2** (16, 5, 17), and the ethers **1b** and **1c**. Thiourea adds slowly. Analogous addition of alcohols to tetracyclone occurs only in an alkaline medium (28).



Hydration is even easier if one of the carboxyls is not esterified [compare with hydration of dibenzoylmalic acid and dibenzoylfumaric acid, which are unknown, contrary to their esters (8)]. As a matter of fact, acid hydrolysis of the ketodiester **2** leads, probably through the keto acid ester **4** and ketol acid ester **5** as intermediates, to the decarboxylation product of the latter, namely to the ketol ester **6b**. The corresponding ketol acid **6a**, to which a different formula was assigned, would then result from the alkaline condensation of benzil and acetone dicarboxylic acid (9).

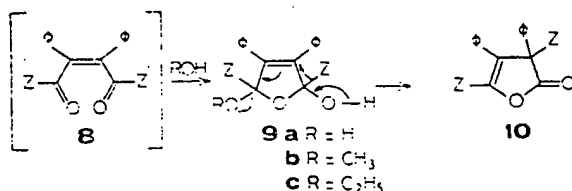


The facility of the two reverse reactions, 1,4-addition to the ketodiester **2** and elimination starting from the ketol-diester **1**, could be one of the reasons for the diversity of the melting points of the ketol-diester **1a** (16, 5, 17). The tautomeric form alcohol-enol-diester **7a** [characterized in the form of ether, **7b** (5)] does not seem to exist in notable proportions according to the NMR spectrum (very slow deuteration of the hydrogen at 5). This permits one to detect the presence of two *cis* and *trans* isomers, one of which is highly dominant.



2) Sensitized photooxidation of the ketodiester 2

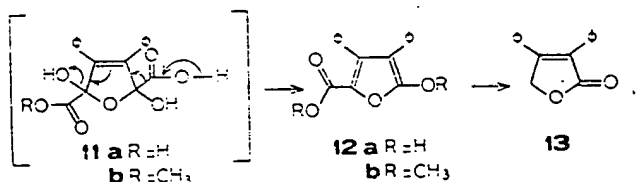
Photooxidation of 2, which is slower than that of tetracyclone, does not give the enedione-diester 8, because hydroxylated compounds (water or alcohols, even diluted ones) add to it very easily. The bis(hemiketal) diester 9a forms in purified dichloromethane or acetone solution and the hemiketal-ketal-diester 9b and 9c form in CH_2Cl_2 that contains a small proportion of the corresponding alcohol. Chloroform containing 0.5% ethanol gives a mixture of 9a and 9c. It is probably difficult to demonstrate the presence of the intermediate peroxide, notably because the reaction is slow [$\text{P}(\text{C}_6\text{H}_5)_3$: photooxidation (10) more rapid than that of 2] or because of the reactivity of 2 toward reducing agents (iodine acetic acid, thiourea: see above).



One cannot obtain the enedione-diester 8 by elimination of water or alcohol from compounds 9. Both by heating and by the action of a dehydrating agent (P_4O_{10}) at ambient temperature, the lactone-diester 10 forms, with migration of a COOCH_3 group. Isomerization of the 1,4-enediones with analogous migration of aryl groups is already known [facilitated by acids (11) and acyl [benzoyl (12)]; migration of alkoxy-carbonyls in an acidic medium in other series is also known (13).

The hydrolysis of the lactone-diester 10, followed by double decarboxylation, gives the lactone (2-furanone) 13, which is also formed by prolonged action of acids on the

bis(hemiketal) diester and its ethers **9**. Reducing agents give the same result in an acidic medium (and not the furane diester which could possibly be formed by reduction).



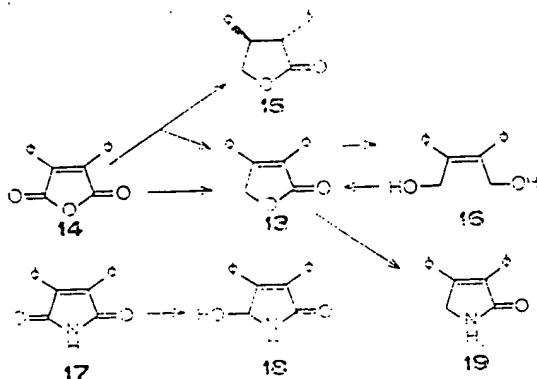
The saponification of the bis(hemiketal) diester **9a** gives first the corresponding mono- and diacid **11b** or **11a**, because acidification of the reaction mixture, followed by methylation with diazomethane, gives the initial substance again. Then hydroxyfuranic acid **12a** is formed, which is unstable (decarboxylation to lactone **13**), but the ether-ester **12b** of it can be isolated by methylation. The same substance is obtained by saponification of the lactone diester **10**, followed by methylation. This lactone diester **10** is perhaps an intermediate in the saponification of the bis(hemiketal) diester **9a** [because migration of COOR or COO⁻ in a basic medium was described (14)], but one cannot demonstrate this. Direct aromatization by elimination of H₂CO₃ in an acidic medium as well as in an alkali medium is probable.

3) Furanone **13**, pyrrolinone **19** and dehydrodimers **22** and **23**

The lactone **13** was obtained by carbonylation of tolane under certain conditions (15). It is prepared by reducing the anhydride **14** with LiAlH₄, over a very short time period. A longer duration gave the diol **16** (15); this is reoxidized with CrO₃ to the lactone **13**. Reduction of the anhydride **14** with KBH₄ (see 18) gives mixtures of lactone **13** and saturated lactone **15** which are difficult to separate; the latter results from a 1,4-addition. The proportion of **13** and **15** varies with the nature of the solvent; the ethylenic lactone **13** is predominant when protic solvents are used and the saturated lactone **15** is favored in aprotic solvents (DMF). In the latter, the low solvation of the BH₄⁻ anion promotes 1,4-addition, which is hindered by the large size of the substituents on the double bond (phenyls).

The analogous reduction of the imide **17** into lactam (2-pyrrolinone) **19** does not occur. However, with KBH₄, one can obtain the hydroxylactam **18**. Very few other similar

reductions of imides were described (19). The lactam **19** is obtained from the lactone **13** by action of ammonium acetate.

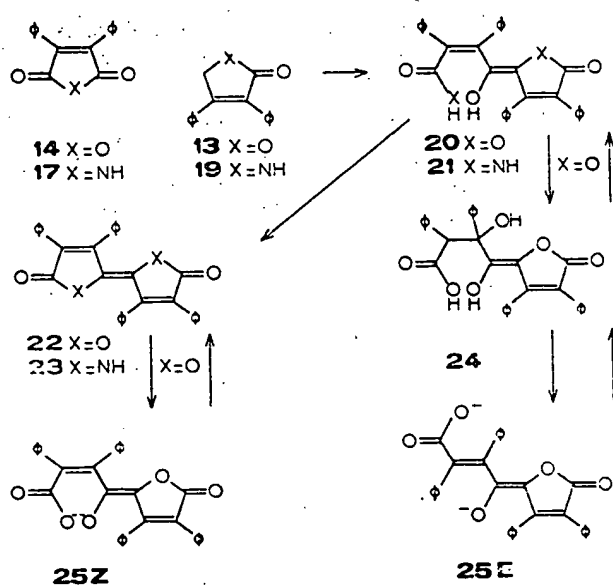


Some ethylenic lactones and lactams that carry a substituent in the 5-position gave dehydrodimers [2,2'-bifurane (or pyrroline)-5,5'-diones; 2,2' single bond] by duplicative oxidation, notably by oxygen or hexacyanoferrate(III) in an alkaline medium (4). Mixtures are formed in the case of lactone **13** and lactam **19**; however, the latter gives a certain quantity of imide **17** by autooxidation in alkali.

One can obtain the dehydrodimers **22** and **23** [$\Delta^{2,2'}$ -2,2'-bifurane (or pyrroline)-5,5'-diones; double bond at 2,2'] by a Perkin-type condensation of lactone **13** and of lactam **19** with anhydride **14** and imide **17**, respectively. An intermediate was isolated in each case. The one that is derived from the lactone **13** is colorless and corresponds to a hydrated product of the expected compound **20** (see par. 1). The formula **24** is assigned to it (or an isomeric formula, with the hydroxyl in the α -position to the carboxyl) based on spectral data. It is easily dehydrated by heating or with acid to the dilactone **22**, which was known (20, 21). Other analogous dilactones were studied, in particular, the hydrolytic opening of one or two lactone rings (23c). The dilactone **22** gives an orange colored solution in a base, probably containing the 25Z anion (see 23c), which regenerates the dilactone **22**, which is yellow, upon acidification. In a basic solution, the intermediate **24** gives a salt, the electronic spectrum of which is very slightly different from that of the preceding salt and which gives **24** again upon treatment with acids; it is assumed that this is the anion **25E**.

The intermediate derived from lactam **19** is orange. Its electronic spectrum being similar to those of the above anions, **25Z** and **25E** (with a bathochromic displacement) it is assigned formula **21**. It is very unstable, dehydrates spontaneously to the dilactam **23**, which is yellow-orange, the *E*-configuration of which is the most probable by analogy to that of dilactone **22** (**21**). Contrary to the dilactones, the dilactams of the type **23** are not very numerous (**24**, **25**).

In conclusion, the presence of two COOCH_3 groups does not inhibit the photooxidation of cyclopentadienone diester **2**. A probable mechanism of degradation has been proposed for the bis(hemiketal) diester **9a** to lactone **13** and a process has also been proposed for obtaining dilactones and dilactams of types **22** and **23**.



EXPERIMENTAL PART

The reactions were followed by thin-layer chromatography (TLC) on fluorescent silica gel and the separations were made by thick-layer chromatography (ThLC) of 1 mm (various eluents). The substances were identified by TLC by the instantaneous melting point and by the IR spectra and possibly with NMR. The melting points were determined on a Kofler block or on a Maquenne block with a gold film. The IR spectra were recorded on KBr pellets (wave number ν in cm^{-1}) and, unless otherwise indicated, the UV spectra were obtained on solutions in ether (wavelength λ in nm, extinction coefficient ϵ in $\text{M}^{-1}\cdot\text{cm}^{-1}$). The NMR spectra were recorded with the aid of Varian HA 100 and Perkin-Elmer R 12 equipment; the solvent was generally CDCl_3 and the internal reference TMS (chemical shift δ in ppm, value rounded to the closest tenth or twentieth of ppm; multiplicity: s singlet, d doublet, t triplet, td resolved triplet, q quadruplet, m multiplet). We wish to thank Madame L. LACOMBE (Collège de France) for the NMR spectra and the Centre de recherches Roussel-Uclaf for the microanalyses.

Methyl 4-hydroxy-3,4-diphenylcyclopentenone-2,5-dicarboxylate, 1a, $\text{C}_{21}\text{H}_{19}\text{O}_6$ (16)

The m.p._{inst} 147-149°C (CHCl_3 or benzene) [147-148°C (16), 136-140°C (17), 139-140°C (5)]. Recrystallization from hot methanol gave a mixture of the ketol 1a and keto-ether 1b. NMR: 7.5-7.2 m (10 aromatic H), 5.0 s (OH), 3.8 s (H at 5), 3.75 s (CH_3), 3.75 s and 3.2 s (CH_3); with D_2O : deuteration of 50% of H at 5 in 2 h; (C_6D_6): 7.6-6.75 m (10 aromatic H), 5.35 s (OH), 3.8 s (H at 5), 3.35 s (0.3 H) and 3.3 s (2.7 H) (CH_3), 3.1 s (2.7 H) and 2.8 s (0.3 H) (CH_3). Rapid photosensitized oxidation (1 h for 200 mg, saturated NaNO_2 filter) in methanol or in a methanol-ether mixture in the presence of triethylamine and rose bengal, with the formation of a complex peroxide mixture (TLC).

Methyl 3,4-diphenylcyclopentadienone dicarboxylate, 2, $\text{C}_{21}\text{H}_{10}\text{O}_3$

The dehydration of ketol 1a (5) is preferably carried out around 0°C. M.p._{inst} 175°C (C_6H_6) [169-175°C (16), 162-167°C (17), 175°C (5)]. UV: λ_{epi} 242 (10,700), λ_{max} 334 (7200), λ_{cp} 420 (750).

Addition of hydroxyl compounds or amines at ambient temperature:

- Water: 1 dg of 2, 20 cm³ of water and 35 cm³ of acetone (3 h); yield 90 mg (86%) of 1a

- Methanol: 117 mg of 2 and 100 cm³ of CH₃OH (25 min), yield 128 mg (100%) of 1b; m.p._{inst} 152°C [146°C (5)]; NMR: 7.5-7.0 m (10 aromatic H), 4.0-3.15 m (h at 5, three CH₃)

- Ethanol: agitation (3 h) of 1 dg of 2 and 40 cm³ of anhydrous ethanol, yield 102 mg (90%) of 1c, m.p._{inst} 127°C [128°C (5)].

- Isopropanol: very slow reaction.

- Allyl alcohol: 3 dg of 2 and 5 cm³ of allyl alcohol; after decoloration and evaporation in vacuum, slow crystallization (1 month) of 102 mg of one of the three reaction products (TLC); m.p._{inst} 151°C (calculated for C₁₇H₂₄O₅: C 75.68, H 5.65, O 18.67; found: C 75.7-75.6, H 5.6-5.8, O 18.7-18.6); IR: ν (C=O) 1770, 1720; NMR (DMSO-CDCl₃ (5:1)): 7.3-6.6 m (10 aromatic H), 4.5-1.6 m (14 H).

- Ammonia: in benzene or dioxane solution, rapid precipitation of mixtures of compounds which were not studied (see 6).

- Thiourea: in acetone solution, slow reaction (15 h).

Methyl 1-acetonyl-3,4-diphenyl-1-cyclopentadienol dicarboxylate, 3

Addition of acetone to the cyclopentadienone 2 does not occur with pure acetone or with acetone containing strong acids (CCl₃CO₂H, CF₃CO₂H), certain salts [Cu(OCOCH₃)₂; NaBr in the presence of CH₃CO₂H] or strong bases (pyridine, aniline, piperidine). Traces of ketol 3 are observed with anhydrous Na and K acetates and triethylamine. Anhydrous sodium iodide gives a yield of 3 to 5%. A mixture of NaI in excess and CH₃CO₂H is the

most suitable. Thus, 0.3 g of the cyclopentadienone 2 and 1 g of anhydrous NaI are dissolved in 40 cm³ anhydrous acetone containing 0.2 cm³ of acetic acid (dried over CuSO₄); a transient brown coloration appeared (visible spectrum; absorption extending beyond 750 nm; disappears upon dilution). After 18 h at ambient temperature, ThLC (CHCl₃ 80%, AcOEt 20%) gives 192 mg (yield 55%) of 3 and approximately 35% of the ketol 1a. M.p._{inst} 100-101°C (ether) (calculated for C₂₄H₂₂O₆: C 70.92, H 5.46, O 23.62; found C 70.9, H 5.5, O 23.5], IR: $\bar{\nu}$ (O-H) 3420, $\bar{\nu}$ (C=O) 1710, 1690, $\bar{\nu}$ (C=C) 1610. UV: λ_{ep} 240 (12,200), λ_{max} 289 (6600), λ_{ep} 315 (5600). NMR: 7.3-6.85 m (10 aromatic H), 4.2 s (OH), 3.7 s (CH₂), 3.6 s (2 OCH₃), 2.2 s (CH₃). Dehydration: slow at ambient temperature in a mixture of CH₃CO₂H with 2% H₂SO₄; at the end of one hour, it gives an orange product (TLC; λ_{max} 345) which changes in solution or on silica, through a blue compound (λ_{max} 630), to two other products; the reaction gives acids at an elevated temperature. Photooxidation: in CHCl₃ with methylene blue, it is slow at ambient temperature and gives a single non-peroxide product; attempts of isolation (ThLC or crystallization) give mixtures of resinous products. Attempts of condensation of cyclopentadienone 2 with acetophenone and pinacolone were unsuccessful.

4-Hydroxy-3,4-diphenylcyclopentenone-2-carboxylic acid, 6a, C₁₈H₁₄O₄ (9)

A mixture of 4.2 g of benzil, 3 g of acetone dicarboxylic acid, 20 cm³ of ethanol and 3.4 g of KOH in 4 cm³ of water is agitated for 6 h at ambient temperature and then allowed to stand for 12 hours; after extraction and washing, the yield is 4.78 g (81%). M.p._{inst} 168°C (ether) [167-168°C (9)]. IR: $\bar{\nu}$ (O-H) 3300, 3100-2400, $\bar{\nu}$ (C=O) 1740, 1685, $\bar{\nu}$ (C=C) 1620. UV: λ_{max} 282. NMR [acetone (D₆)]: 7.6-7.1 m (10 aromatic H), 6.9 s (broad, 2 OH), 3.0 q (CH₂-hydrates, C₁₈H₁₄O₄·H₂O (9): m.p._{inst} 100°C (ether) [100°C (9)] with dehydration and resolidification, then m.p._{inst} 168°C; IR: $\bar{\nu}$ (O-H) 3480, 3370, 3000-2300, $\bar{\nu}$ (C=O) 1710, 1685, $\bar{\nu}$ (C=C) 1630, 1610.

Methyl 4-hydroxy-3,4-diphenylcyclopentenone-2-carboxylate, 6b

1) A solution of diazomethane in ether is added to a solution of 0.23 g of 6a in 10 cm³ of ether, cooled to 0°C; the mixture is evaporated after 5 minutes, yield 225 mg (93%).

2) Reflux (45 min) of a solution of 0.3 g of **2** in 10 cm³ of CH₃CO₂H, 4 cm³ of water and 0.3 cm³ of H₂SO₄; after ThLC (AcOEt 50%, C₆H₁₂ 50%), yield 0.15 g (55%); abundant resins. M.p._{inst} 140-141°C (ether) (calculated for C₁₉H₁₆O₄: C 74.01, H 5.23, O 20.76; found C 74.0, H 5.3, O 20.8). IR: $\bar{\nu}$ (O-H) 3340, $\bar{\nu}$ (C=O) 1735, 1685; $\bar{\nu}$ (C=C) 1620, UV: λ_{\max} 282 (13 800), NMR: 7.5-7.05 m (10 aromatic H), 3.7 s (OCH₂), 3.0 q (OH, CH₂).

Methyl 2,5-dihydroxy-3,4-diphenyl-2,5-dihydrofurane dicarboxylate, 9a

The photooxidation technique was described previously (26); filter: saturated K₂Cr₂O₇. Four tests each with two dg of **2** with 20 mg of methylene blue in 200 cm³ of acetone (duration 15 h, ambient temperature) are combined. After ThLC (AcOEt 45%, C₆H₁₂ 55%), yield 0.56 g (66%). In CH₂Cl₂ (purified with P₄O₁₀; 400 cm³), 4 dg of **2** with 40 mg of methylene blue (17 h, ambient temperature) gives 0.19 (yield 44%). M.p._{inst} 165°C (acetone) (calculated for C₁₀H₁₅O₇: C 64.86, H 4.90, O 30.24; found: C 64.7, H 4.8, O 30.1). IR: $\bar{\nu}$ (O-H) 3460, 3410, $\bar{\nu}$ (C=O) 1755; UV: λ_{\max} 228 (15 500), 263 (9800). NMR (DMSO): 7.6 s and 7.55 s (2 OH), 7.3-7.0 m (10 aromatic H), 3.55 s and 3.45 s (2 OCH₃).

Methyl 2-hydroxy-5-methoxy-3,4-diphenyl-2,5-dihydrofurane dicarboxylate, 9b

Photooxidation of 4 dg of cyclopentadienone **2** with 40 mg of methylene blue in 400 cm³ of pure CH₂Cl₂ containing 1 cm³ of CH₃OH (17 h ambient temperature). After ThLC, (AcOEt 45%, C₆H₁₂ 55%), yield 0.28 g (63%). M.p._{inst} 153°C (ether) (calculated for C₂₁H₂₀O₇: C 65.61, H 5.24, O 29.14; found C 65.3, H 5.3, O 29.0). IR: $\bar{\nu}$ (O-H) 3465, $\bar{\nu}$ (C=O), 1750, 1725. UV: λ_{\max} 228, 262. NMR: 7.5-6.95 m (10 aromatic H), 4.95 s (OH), 3.8 s (OCH₂), 3.7 s (OCH₃), 3.45 s (OCH₃).

Methyl 2-hydroxy-5-ethoxy-3,4-diphenyl-2,5-dihydrofurane dicarboxylate, 9c

Photooxidation (17 h, ambient temperature) of 4 dg of **2** with 40 mg of methylene blue in 400 cm³ of pure CH₂Cl₂ containing 1 cm³ of ethanol. After ThLC (AcOEt 45%, C₆H₁₂ 55%), yield 3 dg (65%). Photooxidation (15 h, ambient temperature) of 2 dg of **2**

with 20 mg of methylene blue in 200 cm³ of CHCl₃ with 0.5% ethanol. After ThLC, yield 57 mg (25%) of **9c** and 96 mg (45%) of **9a**. M.p._{inst} 109°C (ether-pentane) (calculated for C₂₂H₂₈O₇: C 66.32, H 5.57, O 28.11; found C 66.3, H 5.6, O 27.7). IR: $\bar{\nu}$ (O-H) 3470, $\bar{\nu}$ (C=O) 1760, 1745, ϵ_p [?] 1735. UV: λ_{\max} 228, 258. NMR: 7.5-6.95 m (10 aromatic H), 4.9 s and 4.75 s (OH), 3.75 m (CH₂), 3.8 s (OCH₃), 3.7 s (OCH₃), 1.25 m (CH₃).

Methyl 3,4-diphenyl-3-H-2-furanone-dicarboxylate, 10

Dehydration of the bis(hemiketal) **9a** by boiling of its solutions in benzene, dioxane or acetic acid, or by sublimation in vacuum (170°C). Agitation (4 h, ambient temperature) of a suspension of 1 g of P₄O₁₀ in a solution of 140 mg of **9a** in 30 cm³ of benzene; yield 125 mg (94%). Analogous transformations of the ketal hemiketals **9b** and **9c**. M.p._{inst} 171°C (CHCl₃) (calculated for C₂₀H₁₆O₆: C 68.18, H 4.58, O 27.25; found C 68.4, H 4.8, O 26.8). IR: $\bar{\nu}$ (C=O) 1805, 1750, 1730, $\bar{\nu}$ (C=C) 1650. UV: λ_{\max} 260 (6500), $\lambda_{\epsilon p}$ [?] 277 (6000). NMR: 7.4-6.8 m (10 aromatic H), 3.8 s (OCH₃), 3.8 s (OCH₃).

Methyl 5-methoxy-3,4-diphenylfuroate, 12b

1) Saponification of the bis(hemiketal) **9a** gives variable results as a function of time. 15 minutes: mixture of acids not isolated, gives the bis(hemiacetal) **9a** (almost quantitative; absence of the lactone-diester **10**); - 24 h: after treatment with diazomethane, mixture of bis(hemiketal) **9a**, ester **12b** and lactone **13** (absence of **10**); - 31 h: a solution of 0.15 g of **9a** in 10 cm³ of aqueous 1.4 M potassium hydroxide at ambient temperature in a sealed tube under vacuum, after acidification, extraction and treatment with diazomethane at -20°C (10 min) and ThLC (C₆H₆), leads to 67 mg of the ester **12b** (yield 54%) and 25 mg of lactone **13** (yield 26%). Formation of mixtures by action of 1.8 M of CH₃OH-KOH in air.

2) Saponification of 54 mg of lactone diester **10** in 2 cm³ of dioxane, with 6 cm³ of 1.8 M aqueous KOH (42 h, at ambient temperature, in a sealed tube under vacuum), then acidification and methylation with CH₂N₂ at -20°C; yield 18 mg (38%) of ester **12b** and 5 mg (14%) of lactone **13**. M.p._{inst} 178-179°C (CHCl₃) (calculated for C₁₉H₁₆O₄: C 74.01, H 5.23; found C 74.2, H 5.5). IR: $\bar{\nu}$ (C=O) 1705, $\bar{\nu}$ (C=C) 1620, 1610. UV: $\lambda_{\epsilon p}$ [?] 235 (14,600), λ_{\max} 300 (11,600). NMR: 7.4-6.8 m (10 aromatic H), 4.05 s (OCH₃), 3.65 s (OCH₃).

3,4-Diphenyl-5-H-2-furanone, 13, C₁₆H₁₂O₂ (15)

1) A suspension of 3 dg of LiAlH₄ (ether, 40 cm³) is introduced under agitation into a suspension of 0.72 g of anhydride **14** (27) (ether, 50 cm³) followed by agitation for 20 min (decolorization of the yellow solution). After acidification and ThLC (C₆H₆), yield 0.31 g (46%), the diol **16** is separated. 2) Hydrolysis and decarboxylation of the lactone-diester **10** by heating (3 h) of 30 mg of **10** with 3 cm³ of CH₃CO₂H and 0.5 cm³ of 12 M HCl [ThLC; yield 14 mg (70%)], or 87 mg of **10** in 6 cm³ of CH₃CO₂H containing 4 dg of NaI·2H₂O [ThLC; yield 47 mg (80%)]. Hydrolysis and decarboxylation of the bis(hemiketal) **9a** by heating (2.5 h) of 118 mg of **9a** with 5 cm³ of CH₃CO₂H containing 5% H₂SO₄ (ThLC; yield 68 mg (91%)), or by reducing agents in an acidic medium: NaI 0.6 g-CH₃CO₂H 5 cm³, reflux 7 h [yield 0.14 g (73%) starting from 3 dg of **9a**]; HI 2 cm³-CH₃CO₂H 8 cm³ and NaH₂PO₃, ambient temperature, 30 h [yield 76 mg (85%) starting from 0.14 g]; TiCl₃, 15%, 2 cm³ - CH₃CO₂H 5 cm³, ambient temperature, 16 h [yield 34 mg (61%) starting from 88 mg; traces of **9a** and **10**]. Formation of mixtures by the action of acids or reducing agents at ambient temperature. 3) Hydrolysis and decarboxylation of the ester **12b** by heating (1 h) of 15 mg of **12b** with 1.5 cm³ of CH₃CO₂H containing 1% of H₂SO₄; yield 7 mg (61%) after ThCL. Formation of mixtures at ambient temperature (20 h). 4) Oxidation of the diol **16** (97 mg) with CrO₃-pyridine (ambient temperature, 3.5 h); after acidification and ThLC, yield 49 mg (52%). M.p._{inst} 117°C (ether) [115-116°C (15)]. UV: λ_{max} 286 (12,900) [283 (23,500) (15)]. Oxidation of the lactone **13** in dioxane solution or monoglyme with K₃[Fe(CN)₆] in alkaline solution, under nitrogen at ambient temperature, or autooxidation in KOH-CH₃OH solution: very rapid formation of complex mixtures.

Reduction of diphenylmaleic anhydride, 14 with KBH₄

Solid KBH₄ is introduced in 45 minutes into an agitated solution of anhydride **14**; total duration 1 h. After acidification and ThLC (C₆H₆), mixtures of the two lactones are isolated (very difficult to separate these; determination by NMR). The yields do not seem to be improved by longer reduction times.

14	KBH ₄	solvent		yield 13 + 15		% 13	% 15
250 mg	500 mg	CH ₂ OH	20 cm ³	158 mg	(67%) (*)	77	23
250	165	DMF	20	116	(49%) (+)	15	85
250	400	dioxane	15	169	(72%) (x)	68	32
		-H ₂ O	5				

- (*) Although the reaction mixture is colorless (yellow diphenylmaleate), a certain quantity of anhydride **14** is found.
- (+) Formation of three acids, one of which (10%) has m.p._{inst} 175-177°C (ether) (calculated for C₁₆H₁₆O₃: C 74.98, H 6.29, O 18.73; found C 74.7, H 6.3, O 18.1), IR $\bar{\nu}$ (O-H) 3320, 2900, 2620, $\bar{\nu}$ (C=O) 1680, different from the saponification product **15**.
- (x) Several by-products.

trans-3,4-Diphenyl-2-dihydrofuranone, 15, C₁₆H₁₄O₂ (15)

Separation of the mixture of **13** and **15** by crystallization from ether; the lactone **13** crystallizes only from a mixture of ether-pentane (3:1). M.p._{inst} 97-98°C (ether) [94-95°C (15)]. IR: $\bar{\nu}$ (C=O) 1775. NMR: 7.2 s (10 aromatic H), 4.75-3.7 m (4 H). Saponification at 0°C in acid, m.p._{inst} 127-129°C (ether), IR: $\bar{\nu}$ (O-H) 3220, 3000, 2650, $\bar{\nu}$ (C=O) 1690-1710, which gives the lactone **15** again upon standing of its solution in CHCl₃.

2,3-Diphenyl-2-butene-1,4-diol-(Z), 16, C₁₆H₁₆O₂ (15)

Reduction of 173 mg of lactone **13** with 1 dg of LiAlH₄ in 25 cm³ of ether (mixing at 0°C, agitation for 25 minutes at ambient temperature); after acidification and ThLC (AcOEt, 50%, C₆H₁₂ 50%), yield 123 mg (70%). M.p._{inst} 88°C (ether-pentane) [86.5-87.5°C (15)]. NMR: 7.35-6.75 m (10 aromatic H), 4.65 s (2 CH₂), 2.5 s (broad) (2 OH).

5-[1,2 (or 1,3)-dihydroxy-3-carboxy-2,3-diphenylpropylidene]-2-diphenylfuranone, 24

One dg of lactone 13, 0.11 g of anhydride 14, 1 g of 50% NaH and 10 cm³ of THF are mixed in a sealed tube under vacuum. After 3 days at ambient temperature, with intermittent agitation, the mixture is hydrolyzed at 0°C and the ThLC is run in darkness (30% AcOEt, 30% C₆H₁₂ 70%), yield 0.14 g (65%). M.p._{inst} 171-172°C (ether-pentane) (calculated for C₃₂H₂₄O₆: C 76.18, H 4.80; found C 76.1-75.8-76.3, H 4.7-4.6-4.7). IR: $\bar{\nu}$ (O-H) 3480, 3440, broad band up to 2500, $\bar{\nu}$ (C=O) 1760, 1735, $\bar{\nu}$ (C=C) 1635. Visible UV: λ_{\max} 290 (19,500); (18 M CH₃OH-KOH): λ_{\max} 281 (15,200), 410 (25,600); partial regeneration of 24 by acidification (absence of 22). NMR: 7.8-6.6 m (20 aromatic H, 3 OH), 5.7 s (1 OH). Stable in the solid state, unstable in solution in CHCl₃, acetone, alcohols (in light) and DMSO. Formation of mixtures by reaction with CH₂N₂ in ether, or SO₄(CH₃)₂ (four products, 40% of which is represented by 22).

3,4,4',4'-Tetraphenyl- $\Delta^{2,2'}$ -5,5'-bifuranedione, 22 (20,21)

Heating of 24 at 250°C (quantitative) or refluxing (1.75 h) of 107 mg in 10 cm³ of CH₃CO₂H with 5% H₂SO₄, addition of water and washing with methanol and ether; yield 72 mg (73%). Identification with the reduction product of 14 with P(OC₂H₅)₃ (21). Purification by sublimation (280-320°C, 0.3 torr). M.p._{inst} 407-409°C [394-396°C (20), 390°C (21)] (calculated for C₃₂H₂₀O₄: C 82.04, H 4.30, O 13.66; found C 82.1, H 4.3, O 13.7). IR: $\bar{\nu}$ (C=O) 1765, $\bar{\nu}$ (C=C) 1610. Visible UV (CHCl₃ to 0.5% C₂H₅OH): λ_{\max} 415 (42,800) [238 (16,400), 415 (45,400) (20); 403 (21), 399 (45,170) (21)]; (18 M CH₃OH-KOH): λ_{\max} 284 (14,700), 407 (24,500), quantitative regeneration of 22 by acidification. Formation of a complex mixture by heating at 200°C under vacuum with CH₃CO₂NH₄ and C₆H₆.

3,4-Diphenyl-3-pyrrolidin-2-one, 19

Heating of 0.13 g of lactone 13, 1 g of CH₃CO₂NH₄ and 4 cm³ of benzene at 180°C for 16 hours in a sealed tube under vacuum. After addition of water, extraction (CHCl₃) and ThLC (AcOEt 50%, C₆H₁₂ 50%), yield 0.11 g (85%). Purification by sublimation (200°C, 0.2 torr). M.p._{inst} 194-195°C (calculated for C₁₆H₁₃NO: C 81.68, H 5.57, N 5.95, O 6.80;

found C 81.3, H 5.5, N 5.9, O 6.9). IR: $\bar{\nu}(\text{N-H})$ 3175, 3040, $\bar{\nu}(\text{C=O})$ 1680, $\bar{\nu}(\text{C=C})$ $\epsilon_p[?]$ 1640. UV: ($\text{C}_2\text{H}_5\text{OH}$ 95%): λ_{max} 286 (9800). NMR: [acetone (D_6) 90%, DMSO (D_6) 10%]: 7.9 s (broad) (NH), 7.3 s (10 aromatic H), 4.4 s (2 H). Autooxidation in a solution in CH_3OH containing 10% KOH, with the formation of imide 17. Oxidation with $\text{K}_3[\text{Fe}(\text{CN})_6]$ in an alkaline medium under nitrogen of a solution in monoglyme, with the formation of at least seven substances.

5-Hydroxy-3,4-diphenyl-3-pyrrolin-2-one, 18

Agitation at ambient temperature of 1 g of imide 17, 1 g of KBH_4 and 10 cm^3 of CH_3OH for 1 hour. With ThLC (AcOEt 50%, C_6H_{12} 50%), yield 77 mg (77%). Formation of mixtures (absence of lactam 19) for longer reaction durations. M.p._{inst} 216-217°C (acetone) (calculated for $\text{C}_{16}\text{H}_{13}\text{NO}_2$: C 76.47, H 5.22, N 5.57, O 12.74; found C 76.5, H 5.4, N 5.5, O 12.6). IR: $\bar{\nu}(\text{O-H})$ 3370, $\bar{\nu}(\text{N-H})$ 3185, 3050, $\bar{\nu}(\text{C=O})$ 1680. UV: ($\text{C}_2\text{H}_5\text{OH}$ 95%): λ_{max} 226 (19,800), $\lambda_{\text{ep}[?]}$ 251 (8250), λ_{max} 295 (8800). NMR [$\text{DMSO}(\text{D}_6)$]: 8.65 s (NH), 7.4-7.0 m (10 aromatic H), 5.95 t (OH), 5.85 t (H at 5).

5-(1-Hydroxy-3-carbamoyldiphenylallylidene)-2-diphenylpyrrolinone, 21

One dg of the lactam 19, 105 mg of imide 17, 2 dg of 50% NaH and 10 cm^3 of THF are allowed to come into contact for 15 days at ambient temperature with intermittent agitation in a sealed tube under vacuum (development of coloration: light-brown, dark-green, brown-red). After treatment at 0°C and ThLC (AcOEt 50%, C_6H_{12} 50%) 85 mg of 21 (41%) is isolated together with 5 mg (2.5%) of 23 and 19 mg (24%) of 19 (imide 17 not isolated). Orange, M.p. > 250°C (decomposition). Dehydration to the dilactam 23 occurs in the solid state or in solution (CHCl_3) in a few days at ambient temperature. Several analyses correspond to mixtures rich in dilactam 23 (calculated for $\text{C}_{32}\text{H}_{24}\text{N}_2\text{O}_3$: C 79.32, H 4.99, N 5.78; for $\text{C}_{32}\text{H}_{22}\text{N}_2\text{O}_2$: C 82.38, H 4.75, N 6.01; found: C 81.3-81.6-81.8, H 4.9-4.7-4.6, N 5.9-5.8-5.8). IR: $\bar{\nu}(\text{NH}, \text{NH}_2)$ 3190, 3040 (broad band), $\bar{\nu}(\text{C=O})$ 1700, $\epsilon_p[?]$ 1655, 1645. UV: (CHCl_3 with 0.5% $\text{C}_2\text{H}_5\text{OH}$): λ_{max} 318, 435.

3,4,3',4'-Tetraphenyl-5,5'- $\Delta^{2,2'}$ -bipyrrolinedione, 23

Does not form by heating the imide **17** with $\text{P}(\text{OC}_2\text{H}_5)_3$ in vacuum (17 h) (no transformation) (see **22**). Heating of **21** at 250°C in air or sublimation ($250\text{--}330^\circ\text{C}$, 0.35 torr) or boiling of solutions in benzene. Yellow-orange, m.p._{inst} $434\text{--}436^\circ\text{C}$ (CH_2Cl_2); R_f greater than that of **21** (calculated for $\text{C}_{32}\text{H}_{22}\text{N}_2\text{O}_2$: C 82.38, H 4.75, N 6.01; found C 81.6-81.7-81.8-82.0, H 4.8-5.0-4.7-4.7, N 5.8-5.8-5.8-5.9). IR: $\bar{\nu}(\text{N-H})$ 3405, $\bar{\nu}(\text{C=O})$ 1685, $\bar{\nu}(\text{C=C})$ ϵ_p [?] 1650. UV: (CHCl_3 with 0.5% $\text{C}_2\text{H}_5\text{OH}$): λ_{max} 425 (47,000), $\lambda_{\epsilon p}$ [?] 435 (44,600).

Photooxidation of $\text{P}(\text{C}_6\text{H}_5)_3$ (see 10)

Photooxidation (3 min) at ambient temperature (or at -50°C) of 205 mg of $\text{P}(\text{C}_6\text{H}_5)_3$, 2 mg of methylene blue, 10 cm^3 of ether and 90 cm^3 of CHCl_3 . Yield 205 mg (94%) of $\text{OP}(\text{C}_6\text{H}_5)_3$.

REFERENCES

(Translation of French text in the References)

- (27) [not listed in the tables of *Chem. Abstr.* (1942, 36 1592)].